Light Absorption by Soot

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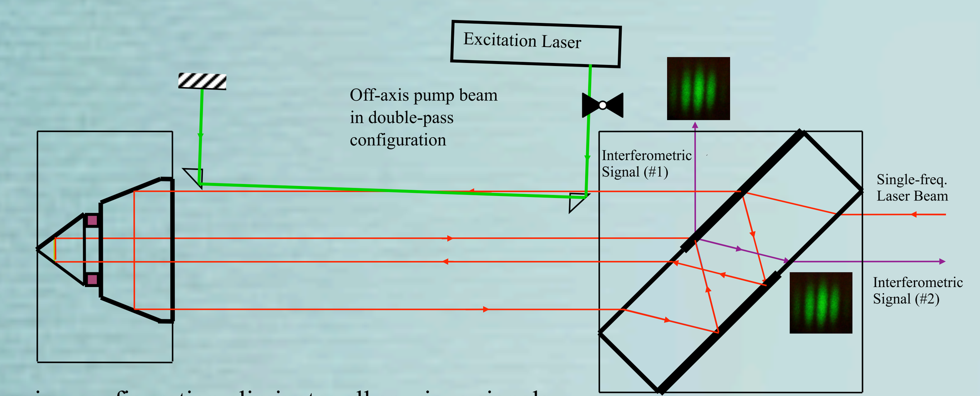
Introduction

Bounding the contribution of light absorption on direct radiative forcing is still very much an active area of research in part because aerosol extinction is dominated by light scattering and in part because the primary absorbing aerosol of interest, soot, exhibits complex aging behavior that can affect its ability to absorb light. In this study, we have used the recently developed technique of photothermal interferometry (PTI) to probe light absorption by soot under a variety of coating conditions as part of the **2008 Boston College-Aerodyne Soot project**.

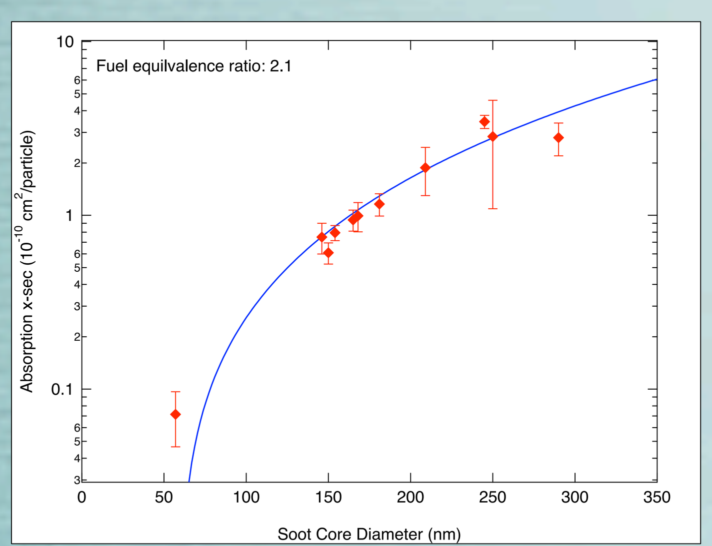
In PTI, the degree of light absorption is measured by monitoring the shift in the interference pattern brought about when the optical pathlength of the "probe" arm is altered, due to the change in the refractive index of air surrounding the particle during heat dissipation. This technique does not suffer interferences from aerosol light scattering and can be calibrated using molecular standards that absorb in the spectral region of interest.



Glancing configuration eliminates all spurious signals

Light absorption by Flat Burner Flame-generated Soot

Plot of light absorption cross-section as a function of furnace-generated soot mobility diameter at a fuel equivalence ratio of 2.1



Diameter (nm)	σ (x10^{-10} cm^2/particle) Soot*	Aquadag^{tm}	Fullerene
150	0.79	---	---
151	---	3.64	---
162	---	---	10.7
165	0.94	---	---
195	---	6.0	---
201	1.81	---	---
250	2.84	10.6	---
322	---	---	18.4

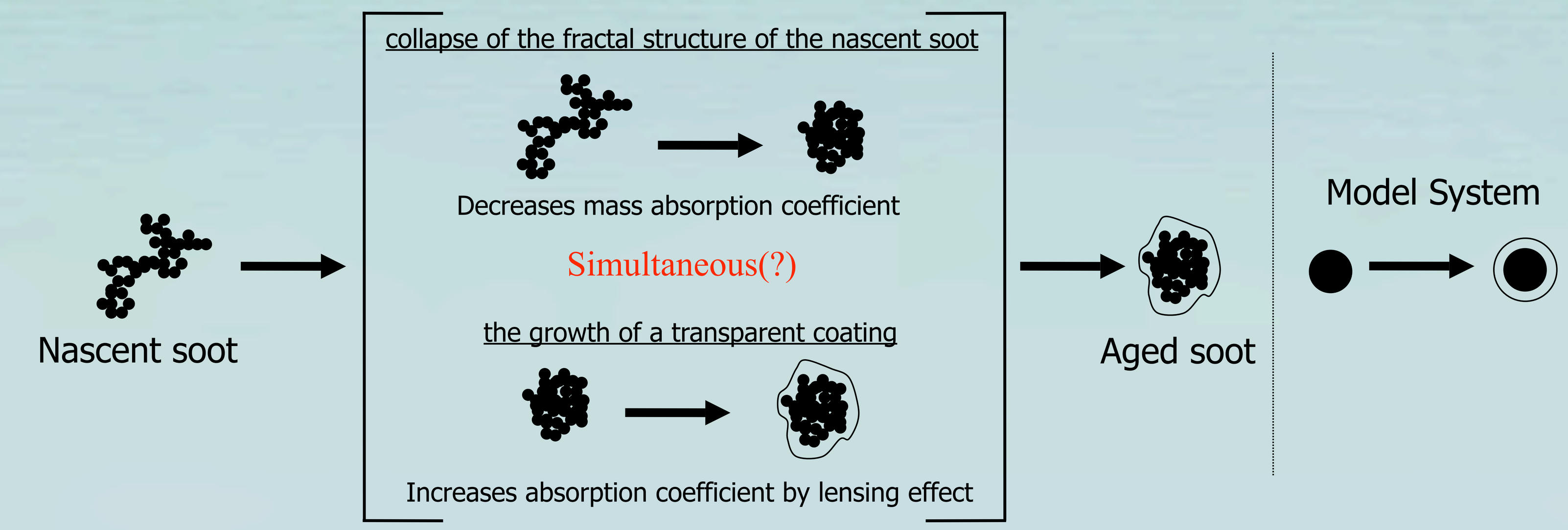
* fuel equiv. ratio: 2.1

Obs. Aquadag ~ 3.7x more efficient light absorption @ 532nm that soot (250 nm)
Obs. Fullerene is ~ 2x more efficient light abs. than Aquadag (162 vs. 151 nm)

Explanation: smaller band-gap in Aquadag (colloidal graphite) and fullerene, compared to soot, gives rise to higher light absorption.

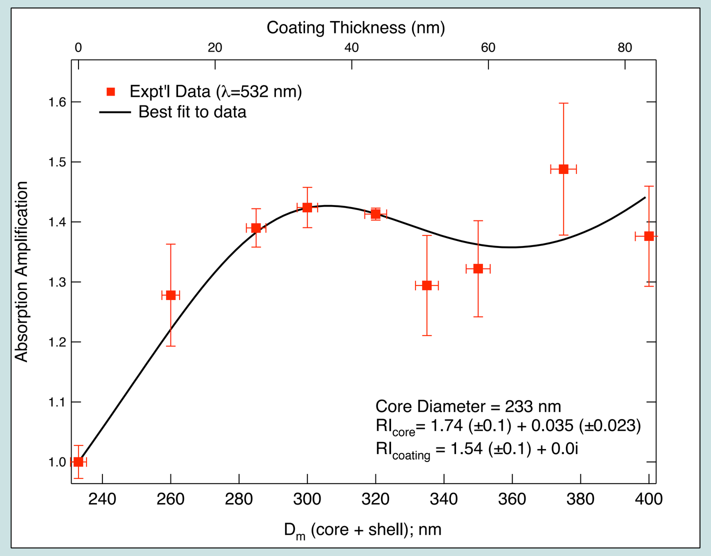
Coating-induced Light Absorption Amplification

Soot aging is typified by the growth of a coating that can encapsulate the aggregate. This non-refractory encapsulant can act as a lens and increase the mass absorption cross-section (MAC) of the coated soot. However, this same encapsulant can, potentially, induce a restructuring of the aggregate to a more compact form that would, in turn, cause a reduction in the MAC (through increased spherule screening).



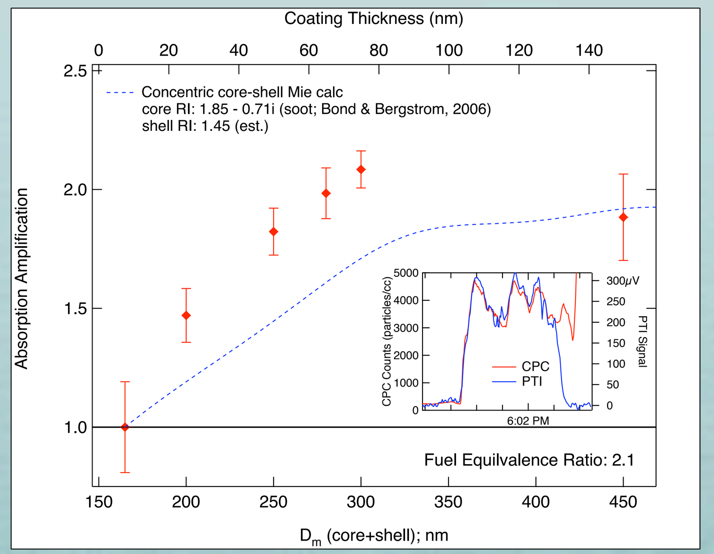
Black-dyed PSL Spheres as a Model System

In an effort to elucidate and quantify these coating effects on soot absorption, we have initiated experiments using a model system that enables us to separately study the coating effect on absorption without fractal collapse. The plot below is of light absorption amplification (ratio of absorption cross-sections for the coated to the uncoated BPSL particle) as a function of dibutyl phthalate (DBP, organic surrogate) coating thickness. Solid line in the plot is the best-fit generated using Mie theory for a concentric core-shell sphere (Mätzler, 2002).



Coating-induced Absorption Amplification in DOS Coated Soot

Shown below is a plot of the measured absorption amplification of flat flame-generated soot as a function of dioctyl sebacate (DOS) shell thickness that was studied during the **2008 Boston College-Aerodyne Soot project**. Light absorption enhancement is seen for all coating thickness, similar to what was observed in the BPSL model system, suggesting no restructuring. The blue line is a concentric core-shell model Mie calculation for a DOS coated, 165 nm diameter soot particle. The experimentally observed higher AA is probably due to the much smaller primary particles, that make up the aggregate, undergoing significant light absorption enhancement relative to a single spherical core. The inset is an example of the PTI signal and CPC number concentration count as a function of time.

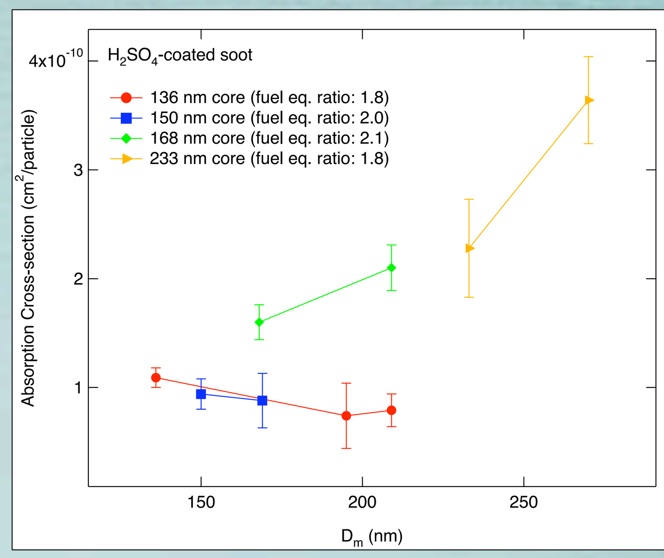


References:

Bond and Bergstrom, (2006) AST 40 27-67
Mätzler (2002) Tech. Rept., Inst. Fur Angew. Phys. Bern.
Sedlacek and Lee, (2007) AST 41 1089-1101

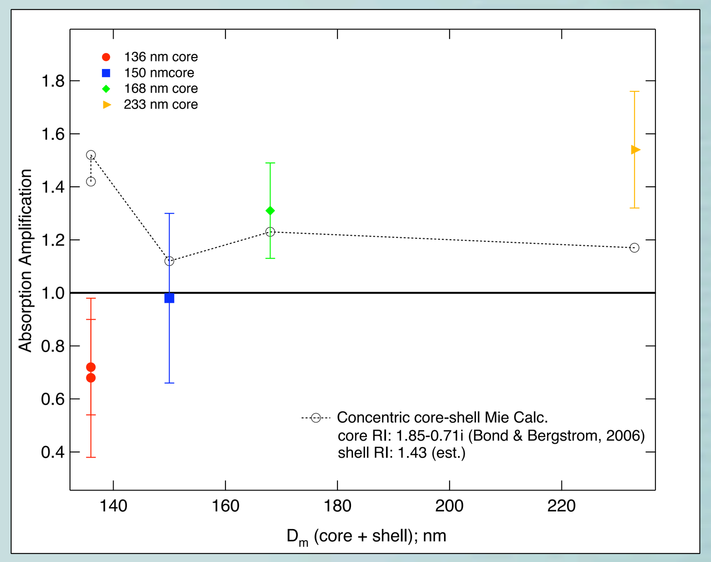
Light Absorption Amplification in H_2SO_4

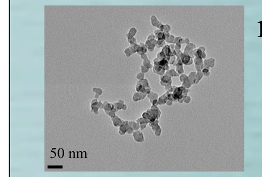
During the **2008 Boston College - Aerodyne Soot Project** sulfuric acid coated soot was also examined. Below is a plot of the measured absorption cross-sections for differing soot 'core' mobility diameters as a function of sulfuric acid coating thickness. Unlike that observed with DOS-coated soot, not all coatings resulted in absorption amplification.



Is Coating-induced Collapse of Aggregate Overrated?

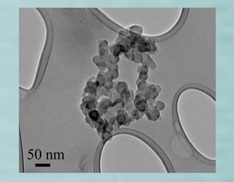
Below is a plot of absorption amplification as a function of the four H_2SO_4 coated core sizes displayed above, along with AA predicted from Mie theory for the same coating thickness for the given core size. These data suggest that the degree of absorption amplification is dependent upon the initial core size: smaller cores showing little to no light absorption enhancement while larger cores exhibiting absorption amplification similar to that seen with DOS-coat soot and the BPSL model system.





nascent soot

Can steric effects prevent complete collapse?



collapsed soot

One *potential* explanation for this behavior is that steric resistance present in the larger fractal aggregates prevent facile collapse because more movement, in the right order, is needed for substantial morphological change to be realized. In contrast, the smaller aggregates suffer less steric hindrance, allowing coating-induced collapse to proceed more freely, offsetting coating-inducing light absorption amplification and giving rise to little or no enhancement in light absorption observed for the smaller particles.

Light Absorption of H_2SO_4 Coated Soot as a Function of RH

150 nm core			233 nm core		
% RH	σ (x10^{-10} cm^2/particle)	AA	% RH	σ (x10^{-10} cm^2/particle)	AA
5	0.9 ± 0.3	---	5	1.9± 0.25	
25	1.0± 0.3	1.1	65	2.0 ± 0.36	1
50	0.7 ± 0.3	0.82	---	---	---

Conclusions:

- Coating-induced absorption amplification experimentally observed with DOS-coated soot.
- Preliminary findings with H_2SO_4 coated soot suggests that the initial aggregate size/morphology may play an important role on the degree of restructuring that can be induced by the coating material.

Acknowledgements

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